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SEMICONDUCTOR/SOLID ELECTROLYTE JUNCTIONS FOR OPTICAL  
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A F SAMMELLS 14 SEP 86 N00014-84-C-0723

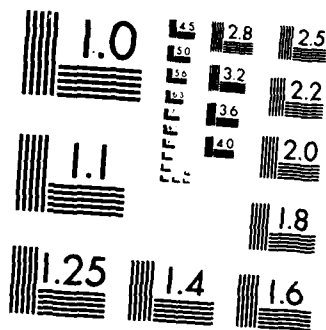
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The program was directed towards characterization of electrode and photoelectrode solid-state junctions with solid polymer electrolytes (SPEs) possessing incorpor- ated electrochromic materials. Excellent electrochemical reversibility and corresponding electrochromic phenomena were found for cells utilizing lutecium diphthalocyanine and heptyl viologen as incorporated electrochromic materials.		

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FINAL REPORT SUMMARY ONR N00014-84-C-0723

Solid-state electrochromic cells of the general configuration:

Lutecium Diphthalocyanine	Poly(Amps)	Nafion	Poly(Amps)	SnO <sub>2</sub> cond.
on SnO <sub>2</sub> cond. glass	+ SE	117	+ CeCl <sub>3</sub>	glass

were prepared using the supporting electrolytes (SEs) 0.1M Na<sub>2</sub>SO<sub>4</sub> and 0.1M KCl. Upon subjecting the cell to anodic and cathodic voltage scans, up to four distinct color changes were observed varying from red (at anodic potentials) to violet (at cathodic potentials). Formation of the violet lutecium diphthalocyanine reduction product was not found to be contingent upon the absence of alkali cations as reported by others.

For the electrochromic cell:

SnO <sub>2</sub>	/	Poly(Amps)	/	Nafion	/	Poly(Amps)	/	SnO <sub>2</sub>
glass		+ HV <sup>2+</sup>		117		+ CeCl <sub>3</sub>		glass
		+ NaPF <sub>6</sub>				+ NaPF <sub>6</sub>		

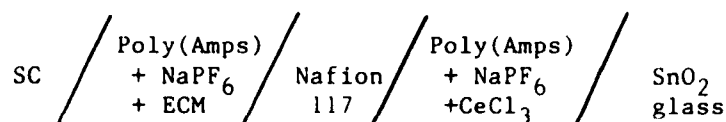
in which the heptyl viologen (HV<sup>2+</sup>) working electrode compartment was subjected to a cathodic scan, two distinct reduction peaks were observed at respectively -1.74 and -1.90V versus the CeCl<sub>3</sub>/SnO<sub>2</sub> reference/counter electrode. This corresponded to the formation of respectively, the radical and diradical cation species of HV<sup>2+</sup>. This electrochromic cell was found to be highly electrochemically reversible as monitored by a He/Ne laser beam (583nm) transmitted through the bulk of this semi-transparent thin film solid-state cell.

The dependency of n-TiO<sub>2</sub> flatband potential (V<sub>fb</sub>) for cells of the general configuration: n-TiO<sub>2</sub>/Nafion 117, Redox species/SnO<sub>2</sub> conducting glass, was systematically studied for the redox species Ru(bpy)<sub>3</sub><sup>2+</sup>, Fe(bpy)<sub>3</sub><sup>2+</sup> and Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> as a function of their concentration within the polymer. A linear relationship V<sub>fb</sub> = M (1/concentration) + b was found to hold for all cells. The slope (M) was found dependent upon metal complex used and its oxidation state. The sensitivity of the measured n-TiO<sub>2</sub> flatband potential to its immediate chemical environment at its interface with the redox polymer can be a strategy pursued for chemical detection.

Solid-state photoelectrochromic cells possessing the general configuration:

SC	/	Poly(Amps)	/	Nafion	/	Poly(Amps)	/	SnO <sub>2</sub>
		+ NaPF <sub>6</sub>		117		+ NaPF <sub>6</sub>		glass
		+ ECM				+ CeCl <sub>3</sub>		

Solid-state photoelectrochromic cells possessing the general configuration:



where SC = n-TiO<sub>2</sub> or n-CdS and ECM = HV<sup>2+</sup> or LuH(Pc)<sub>2</sub> were prepared. SPE/SC junctions containing dispersed HC<sup>2+</sup> behaved in a somewhat analogous manner to liquid junction PEC cells. Those cells prepared with LuH(Pc)<sub>2</sub> directly deposited onto the semiconductor surface had these photoelectrochemical properties dictated by the SC/LuH(Pc)<sub>2</sub> solid-state junction rather than by SPE redox properties.

TECHNICAL REPORTS SUBMITTED TO ONR DURING THIS CONTRACT (N00014-84-C-0723)

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0001 AG	January 15, 1986
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0001 AJ	September 14, 1986

JOURNAL ARTICLES EMANATING FROM THIS CONTRACT:

S. K. Schmidt, R. L. Cook and A. F. Sammells, "Semiconductor Redox Polymer Detector Junctions," J. Electrochem. Soc., 133, 1617 (1986).

A. F. Sammells and N. U. Pujare, "Electrochromic Effects on Heptylviologen Incorporated Within a Solid Polymer Electrolyte Cell," J. Electrochem. Soc., 133, 1270 (1986).

A. F. Sammells and N. U. Pujare, "Solid-State Electrochromic Cell Using Lutecium Diphthalocyanine," J. Electrochem. Soc., 133, 1065 (1986).

R. L. Cook and A. F. Sammells, "Investigation of Photoelectrode Redox Polymer Junctions," J. Electrochem. Soc., 132, 2429 (1985).

A. F. Sammells and S. K. Schmidt, "A Two-Photoelectrode Solid-State Photoelectrochemical Cell," J. Electrochem. Soc., 132, 520 (1985).

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